In situ electrical resistance and activation energy of solid C_{60} under high pressure*

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The *in situ* electrical resistance and transport activation energies of solid C_{60} fullerene have been measured under high pressure up to 25 GPa in the temperature range of 300–423 K by using a designed diamond anvil cell. In the experiment, four parts of boron-doped diamond films fabricated on one anvil were used as electrical measurement probes and a W–Ta thin film thermocouple which was integrated on the other diamond anvil was used to measure the temperature. The current results indicate that the measured high-pressure resistances are bigger than those reported before at the same pressure and there is no pressure-independent resistance increase before 8 GPa. From the temperature dependence of the resistivity, the C_{60} behaviors as a semiconductor and the activation energies of the cubic C_{60} fullerene are 0.49, 0.43, and 0.36 eV at 13, 15, and 19 GPa, respectively.

Keywords: high pressure, electrical resistance, activation energy, C_{60} fullerene

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1. Introduction

As one of the allotropes of carbon, much attention has been paid to the electrical transport properties of C_{60} fullerene since its discovery.[1–7] The investigation of the high-pressure *in situ* electrical resistance of the materials helps us to understand the transport properties of the carriers under high pressure, while from the viewpoint of activation energy, the defect/impurity level between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (HUMO) can be studied under high pressure. In 1992, Saito *et al.*[3] measured the electrical resistance and band gap of solid C_{60} under high pressure; they used a 2-termianal method in an MA8-type apparatus driven by two RH3-type guide blocks in a uniaxial 2000-ton hydraulic press. In addition, they used a conventional digital multimeter with the upper measurable limit (20 MΩ) for electrical resistance measurement. The purity of C_{60} was 99%. From the experiment results, they observed the resistance rise slowly up to around 8 GPa and decrease steeply with increasing pressure. The resistance attained a minimum at around 20 GPa and then started to rise again. In 2006, Qiu *et al.*[4] remeasured the high-pressure *in situ* resistance of C_{60}; they conducted their experiments in a four-probe-designed diamond anvil cell (DAC). The C_{60} sample used in the experiments was sublimed fullerene powder from Alfa Aesar with purity above 99.95%. They did not observe that the electrical resistance increases with pressure increasing from ambient to 8 GPa, instead they observed the continue decrease of the resistance with increasing pressure up to 21 GPa. It is known that the difference between the electrical resistance results in Refs. [3] and [4] can be due to different experimental conditions on compression. The authors conclude three features as follows. (1) The purity of the sample. The existence of solvents such as toluene and hexane will influence the electrical measurement results.[3] (2) The electrode configuration. In Saito and Manabu's experiments,[3] 2 metal wires was used as the electrical measurement probes. While in Qiu *et al*'s experiments,[4] four-probe method was used. As we know, the position of the wires in the sample will change with applied pressure, which may lead to less electrical measured errors forming in the 4-terminal method than in the 2-terminal method. (3) The low upper measurable limit of the multimeter for electric resistance measurement will influence the judgment of researchers.

In this paper, before the experiment, the cubic C_{60} sample was pretreated so as to eliminate the negative effects of the purities such as toluene and hexane. In order to eliminate negative effects of the electrode position changes, heavily boron-doped diamond film with a van der Pauw configuration deposited on one diamond anvil was used as electrodes. A digital multimeter with the high upper measurable limit (100 TΩ) was used for electrical resistance measurement. Furthermore, the oxygen will enter into the solid C_{60}, forming impurity levels between the HOMO and the HUMO when exposed the air.[8,9] In order to investigate the impurity properties in the

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sample, temperature dependence of resistivity measurement experiments was conducted, and a standard W–Ta thin film thermocouple which was integrated on the diamond anvil was used to accurately measure the high-pressure *in situ* temperature.

2. Experimental details

A Mao–Bell type DAC with the anvil culet of 400 μm in diameter was utilized to generate high pressure. A sheet of T-301 stainless steel used as a gasket was indented to 40 μm in thickness. A hole with 200 μm in diameter was drilled in the center of the indentation by a laser drilling machine and served as a sample chamber. A piece of ruby crystal with the size of 5 μm was used as the pressure calibrator.[10] The section profile of the designed DAC is displayed in Fig. 1. Heavily boron-doped diamond film was deposited on the lower diamond anvil and then patterned into van der Pauw configuration as electrodes. The electrode manufacturing process has been reported in our previous work.[11,12] To insulate the diamond electrodes from the metal gasket and to insulate the sample from metal gasket under high pressure, diamond powder mixed with epoxy was used. The temperature experiment was carried out by placing the DAC into a warm drying cabinet and the temperature was measured using a standard W–Ta thin film thermocouple which was integrated on the upper diamond anvil.[13]

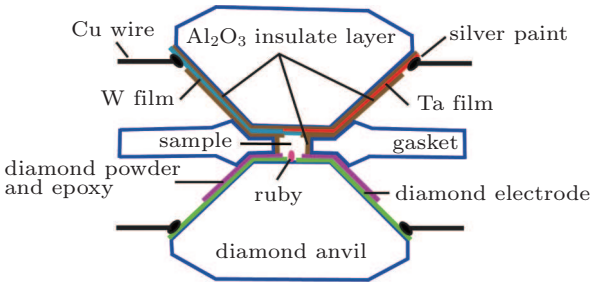


Fig. 1. (color online) Section profile of the designed DAC.

The C_{60} powder sample was purchased from Alfa Aesar Co. with 99.95% purity. Before the experiment, the powder of C_{60} obtained after evaporating the eluant of pure C_{60} fraction with a rotary evaporator was heated up to 200 °C for a few hours under vacuum to evaporate solvents such as oxygen, toluene, and hexane. A bulk single crystal with a dimension 10×20 μm^2 was used in the experiment and the scanning electron microscopy (SEM) images of the bulk C_{60} are displayed in Fig. 2.

The high-pressure electrical resistance was measured by Solartron 1260 impedance analyzer equipped with a Solartron 1296 dielectric interface. The upper measurable limit of the resistance was 100 TΩ. In the temperature experiments, the electrical current was provided by a Keithley 2400 Source Meter, and the voltage drop was measured using a Keithley 2700 Multimeter.

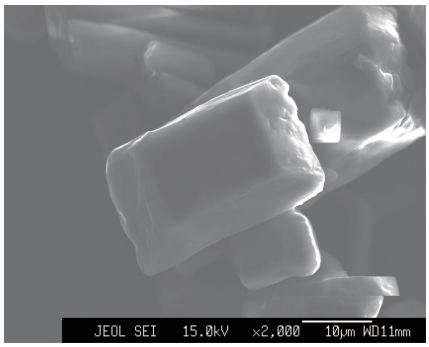


Fig. 2. SEM images of the powder C_{60}.

3. Results and discussion

The pressure dependence of C_{60} fullerene sample resistances at room temperature are shown in Fig. 3. From ambient pressure to 5 GPa, the electrical resistances of the bulk single crystal C_{60} are bigger than 100 TΩ, which indicates the sample is almost an electrical insulator before 5 GPa. With increasing applied pressure, the electrical resistances decrease steeply, and reach a minimum at around 20.2 GPa. Under high pressure and high temperature conditions, C_{60} is known to undergo polymerization. Below 32 GPa and 800 K, several kinds of one-, two-, and three-dimensional polymeric phases of C_{60} have been reported[14] Even at room temperature, the face-centered cubic (fcc) phase of C_{60} molecules could polymerize in the form of disorder states arising from nucleation of molecular chains in random directions because of the quasi-free molecular rotation with increasing applied pressure.[15] In our experiments, the initial C_{60} sample is a molecular crystal in which C_{60} molecules are arranged in an fcc structure and are bound together by weak van der Waals forces.[16] The electron transport through the molecular bonds is very weak which makes the electrical insulation of the solid C_{60} at relatively lower pressure. However, with increasing applied pressure, the individual molecules are bound together into pairs or larger clusters by covalent intermolecular bonds because of polymerization which makes the electron transport easier.[15] Thus, the pressure-induced polymerization is one possible cause of the steep pressure-dependent decrease in electrical resistance observed in Fig. 3. Furthermore, under compression, the electronic conduction of an organic semiconductor is dominated by electrons excited from the HOMO to the HUMO, impurity level, or other levels in the gap such as strain-induced level. Both pressure-induced bandgap shrinkage and strain-induced level can be another reason of the resistance decrease of solid C_{60} from ambient pressure to 20.2 GPa.

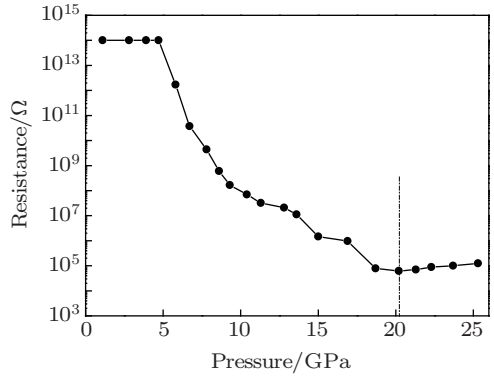


Fig. 3. Pressure dependence of C_{60} fullerene sample resistance. Solid circles denote the compression process. The solid dashed line shows the location of the phase transition point.

Generally, the structure transitions of a material can affect its electrical properties.[17] At ambient conditions and high pressure, the pressure-induced phase transitions have been well studied before. The results indicated that there is no sign of phase transitions at 8 GPa and the C_{60} cages collapse and form an amorphous phase of carbon at 16–20 GPa.[18–20] As shown in Fig. 3, when the applied pressures are higher than 20.2 GPa, the slow electrical resistance increase is observed till the pressure reaches up to 25 GPa. The electrical resistance increases can be attributed to the collapse of the C_{60} cage and the formation of an insulating amorphous phase at 20.2 GPa.[21]

Comparing the results in Fig. 3 in this paper to the results reported in Ref. [3], two differences can be found. (1) There is no electrical resistance increase with increasing applied pressure up to 8 GPa, instead the resistance continues to decrease till it reaches 61.5 KΩ at 20.2 GPa. (2) The high-pressure *in situ* electrical resistance measured in this experiment is bigger than the results reported in Ref. [3] at the same pressure. Since there is no pressure-induced phase transition at 8 GPa, the possible reasons for the above two discrepancies can be due to different experimental conditions. (1) The higher purity of the sample used in this experiment than that in Ref. [3]. That is the reason why smaller electrical resistance is observed at the same pressure in the whole experimental process. (2) The upper resistance measurable limit reported in Ref. [3] was 20 MΩ, and the measurable resistance range of the instrument is not enough to meet the demand before 8 GPa. (3) Because the 2-terminal method was used in Ref. [3], both the change of the contact point between the metal wires and the sample and the variation of the sample shape under high pressure may lead to the measured electrical resistance increase before 8 GPa. The current results have similar variation trend with the results reported in Ref. [4], except the high-pressure *in situ* electrical resistances are at least two orders of magnitude bigger at the same pressure. The reason can be attributed to the pretreatment of the sample with the pure sample, and the solvents such as toluene and hexane have been evaporated in this experiment.

At higher temperatures, the carrier concentration is determined by the intrinsic properties of the pure semiconductor crystal. While at low temperatures, the concentration of carriers is affected by the impurity and/or the defect content. For investigating the defect/impurity properties in the solid C_{60} before the phase transition, the temperature dependence of C_{60} resistivity were measured in the temperature range of 300–423 K at different pressures. The results are plotted in Arrhennius format and shown in Fig. 4. It can be seen that below 20 GPa the resistivity of C_{60} increases with increasing temperature, and therefore the C_{60} exhibits semiconductor behavior[22] From the temperature dependence of resistivity, transport activation energy of C_{60} at a given pressure could be obtained according to the equation

$$\rho = \rho_0 \exp(E_g/2k_B T), \tag{1}$$

where ρ_0 is the starting resistivity at ambient conditions, E_g is the transport activation energy, k_B is Boltzmann's constant, and T is the temperature. According to Eq. (1), the value of E_g was obtained by linearly fitting the plot of $\ln\rho$ versus $1000/T$. The transport activation energy is derived as follows: 0.49, 0.43, and 0.36 eV at 13, 15, and 19 GPa, respectively.

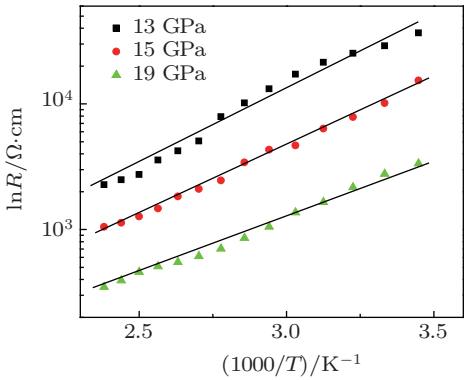


Fig. 4. (color online) Characteristics of $\ln\rho$ versus $1000/T$ of C_{60} under different pressures.

4. Conclusions

The high-pressure *in situ* electrical resistance and transport activation energy of cubic C_{60} has been measured in this paper. Both boron-doped diamond electrodes and a standard W–Ta film thermocouple fabricated on the diamond anvil have been used in the experiment. The current results have evidenced that there are no electrical resistance increases with increasing applied pressure from ambient to 8 GPa. The authors also explained the reason for the discrepancies of the previous reported experiment results. From the temperature dependence of resistivity measurement results, the transport activation energy is derived as follows: 0.49, 0.43, and 0.36 eV at 13, 15, and 19 GPa, respectively.

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